Synthesis and Structures of Two Triorganotin(IV) Polymers R3SnO2CC6H4[N=C(H)C(CH3)CH(CH3)-3-OH]-pn (R = Me and Ph) Containing a 4-[(2Z)-(3-Hydroxy-1-methyl-2-butenylidene)amino] benzoic Acid Framework

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1 Introduction

Schiff bases containing organotin(IV) moieties have received increasing attention owing to their potential applications in medicinal chemistry and biotechnology [1–9]. In particular, the organotin(IV) derivatives of Schiff bases containing amino acetate skeletons have demonstrated diverse structural possibilities [10–18] and cytotoxic potential [8, 17, 18]. A common obstacle in the work is the synthesis of Schiff bases in the form of free acids and hence their sodium or potassium salts are frequently used for the reactions which are stable only for a short period. To overcome this difficulty, we recently synthesized a stable Schiff base in the form of the acid, 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoic acid (LHH′), which has been characterized crystallographically and some of its organotin(IV) complexes have been reported [19]. As a continuation of our previous work in this area, we report the synthesis and characterization of two new polymers viz., $[Me_3Sn(LH)]_n$ (**1**) and $[Ph_3Sn(LH)]_n$ (**2**) containing the ligand LH bridging two triorganotin moieties through both carboxylate and hydroxide groups. The complexes have been characterized in the solid state by means of ^{119}Sn Mössbauer and IR and in solution by ^1H, ^{13}C and ^{119}Sn NMR spectroscopic techniques. The crystal and molecular structures of both the triorganotin(IV) complexes (**1**–**2**) are also reported in order to bestow deeper insight into their coordination geometry. The structural parameters of the polymers are compared with those of related compounds mimicking the organotin repeat units.

2 Experimental Section

2.1 Materials

Me_3SnCl (Merck), Ph_3SnCl (Fluka AG), acetylacetone (Sisco) and *p*-aminobenzoic acid (Hi Media) were used as such. The solvents used in the reactions were of AR grade and were dried using standard procedures.

2.2 Physical Measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referred to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. The Mössbauer spectra were recorded with a conventional spectrometer operating in the transmission mode. The source was $Ca^{119}SnO_3$ (Ritverc GmbH, St. Petersburg, Russia; 10 mCi), moving at room temperature with constant acceleration in a triangular waveform. The driving system was obtained from Halder (Seehausen, Germany), and the NaI (Tl) detector from Harshaw (De Meern, The Netherlands). The multi-channel analyser and the related electronics were purchased from Takes (Bergamo, Italy). The solid absorber samples, containing ca. 0.5 mg cm^{-2} of ^{119}Sn, were held at 77.3 K in a MNC 200 liquid-nitrogen cryostat (AERE, Harwell, UK). The velocity was calibrated using a ^{57}Co Mössbauer source (Ritverc GmbH, St. Petersburg, Russia, 10 mCi), and an iron foil as absorber. The isomer shifts are relative to room temperature $Ca^{119}SnO_3$.

2.3 Synthesis of 4-[(2*Z*)-(3-Hydroxy-1-methyl-2-butenylidene)amino]benzoic Acid (LHH′) and its Sodium Salt (LHNa)

The 4-[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)amino]benzoic acid (LHH′) and its sodium salt (LHNa) were prepared as described in our earlier report [19].

2.4 Synthesis of the Triorganotin(IV) Complexes

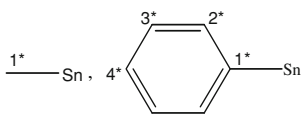
*2.4.1 Synthesis of $[Me_3Sn(LH)]_n$ (**1**)*

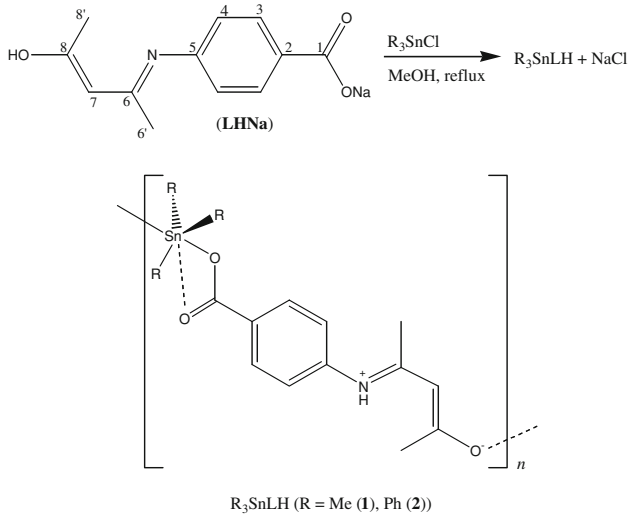
A warm solution of LHNa (0.42 g, 1.75 mmol) in anhydrous methanol (ca. 10 mL) was added drop-wise to a solution of Me_3SnCl (0.35 g, 1.75 mmol) in anhydrous methanol (ca. 20 mL) under stirring conditions. The reaction mixture was refluxed for 5 h and then filtered while hot. The filtrate was then evaporated to dryness, washed thoroughly with hexane and dried in vacuo. The dried mass was extracted into chloroform (ca. 20 mL) and filtered. The filtrate was allowed to evaporate at room temperature giving a pale yellow solid. Re-crystallization of the product from dichloromethane/hexane (v/v 1:1) mixture afforded pale yellow crystals of **1** in 65% (0.43 g) yield. M.p.: 133–135 °C. Elemental analysis (%), Calcd. for $C_{15}H_{20}NO_3Sn$: C 47.29, H 5.29, N 3.68; Found: C 47.61, H, 5.46, N 3.92. IR (cm^{-1}): 1636 $\nu(OCO)_{asym}$, 1594 ν(C=N), 1311 ν(Ph(CO)). ^{1}H NMR ($CDCl_3$) δ_H: Ligands skeleton: 12.61 (brs, 1H, OH, D_2O exchangeable), 8.01 (d (8.5 Hz), 2H, H4), 7.11 (d (8.5 Hz), 2H, H3), 5.24 (s, 1H, H7), 2.08 and 2.11 (s, 6H, H6′ and H8′); Sn–Me skeleton: 0.64 (s, 9H) [$^{2}J(^{1}H–^{119}Sn) = 57$ Hz], ppm. ^{13}C NMR ($CDCl_3$) δ_C: Ligand skeleton: 196.6 (C1), 170.9 (C6), 158.9 (C8), 142.4 (C5), 131.3 (C4), 128.3 (C2), 122.8 (C3), 98.9 (C7), 29.2 (C6′), 20.1 (C8′); Sn–Me skeleton: −2.26 (C1*) [$^{1}J(^{13}C–^{119}Sn) = 390$ Hz], ppm. ^{119}Sn NMR ($CDCl_3$ solution): 133.9, ppm. ^{119}Sn Mössbauer: $\delta = 1.31$, $\Delta = 3.34$, $\Gamma\pm = 0.83$ mm s^{-1}, $\rho = 2.55$.

*2.4.2 Synthesis of $[Ph_3Sn(LH)]_n$ (**2**)*

This compound was prepared in the same manner as described for **1** by using Ph_3SnCl (0.50 g, 1.30 mmol) and L^1HNa (0.31 g, 1.30 mmol). After work-up, the crude product was re-crystallized from dichloromethane/hexane mixture which upon slow evaporation afforded a pale yellow crystalline product of **2** in 77% (0.57 g) yield. M.p.: 163–164 °C. Elemental analysis (%), Calcd. for $C_{30}H_{27}NO_3Sn$: C 63.41, H 4.79, N 2.46; Found: C 63.74, H 5.05, N 2.57. IR (cm^{-1}): 1636 $\nu(OCO)_{asym}$, 1594 ν(C=N), 1322 ν(Ph(CO)). ^{1}H NMR ($CDCl_3$) δ_H: Ligand skeleton: 12.62 (brs, 1H, OH, D_2O exchangeable), 8.09 (d (8.5 Hz), 2H, H4), 7.10 (d (8.5 Hz), 2H, H3), 5.23 (s, 1H, H7), 2.08 and 2.10 (s, 6H, H6′ and H8′); Sn–Ph skeleton: 7.78–7.80 (m, 6H, H2*), 7.45–7.47 (m, 9H, H3* and H-4*), ppm. ^{13}C NMR ($CDCl_3$) δ_C: Ligand skeleton: 196.8 (C1), 171.9 (C6), 158.6 (C8), 143.0 (C5), 131.8 (C4), 126.8 (C2), 122.6 (C3), 99.2 (C7), 29.3 (C6′), 20.1 (C8′); Sn–Ph skeleton: [$^{n}J(^{13}C–^{119}Sn$, Hz)]:138.4 (C1*) [625], 136.9 (C2*) [45], 130.1 (C4*) [15], 128.9 (C3*) [60], ppm. ^{119}Sn NMR ($CDCl_3$ solution): −111.5 ppm. ^{119}Sn Mössbauer: $\delta = 1.29$, $\Delta = 2.88$, $\Gamma\pm = 0.93$ mm s^{-1}, $\rho = 2.23$.

For the ^{1}H- and ^{13}C- NMR assignments, refer to Scheme 1 for the numbering scheme of the ligand skeleton, while for the Sn–R skeleton, the numbering is as shown below:





Scheme 1 Syntheses and structure of triorganotin(IV) complexes (**1** and **2**)

2.5 Crystal Structure Determinations

Crystals of compounds (**1** and **2**) suitable for an X-ray crystal-structure determination were obtained from dichloromethane/hexane solutions of the respective compounds. All measurements were made using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a Nonius KappaCCD diffractometer [20] and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [21]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method [22] was applied. The space groups in **1** and **2** were uniquely determined by the systematic absences. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and views of segments of the polymeric structures are shown in Figs. 1 and 2.

The structure of **1** was solved by direct-methods using SIR92 [23]. The structure of **2** was solved by heavy-atom Patterson methods [24], which revealed the position of the Sn-atom, and all remaining non-hydrogen atoms were located in a Fourier expansion of the Patterson solution, which was performed by DIRDIF94 [25].

The asymmetric unit of compound **1** contains one independent chemical repeat unit from each of two symmetry-independent polymeric chains, while just one such repeat unit is in the asymmetric unit of **2**. The non-hydrogen atoms were refined anisotropically. The H-atoms of the protonated imine groups of the ligands were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups). The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied for **1** and **2**. Three reflections in **1** and five reflections in **2** whose intensities were considered to be extreme outliers, were omitted from the final refinement. Calculations were performed using the SHELXL97 program [26].

Table 1 Crystallographic data and structure refinement parameters for **1** and **2**

	1	**2**
Empirical formula	$C_{15}H_{21}NO_3Sn$	$C_{30}H_{27}NO_3Sn$
Formula weight	381.93	568.15
Crystal size (mm)	0.25 × 0.25 × 0.28	0.22 × 0.35 × 0.38
Crystal shape	Prism	Prism
Temperature (K)	160(1)	160(1)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a (Å)	18.5011(2)	16.3971(2)
b (Å)	8.9487(1)	17.1164(3)
c (Å)	20.1879(2)	18.1996(2)
β (°)	104.0489(8)	90
V (Å^3)	3242.35(6)	5107.9(1)
Z	8	8
D_x (g cm^{-3})	1.565	1.477
μ (mm^{-1})	1.581	1.031
Transmission factors (min, max)	0.607, 0.680	0.690, 0.801
$2\theta_{max}$ (°)	60	60
Reflections measured	74358	69769
Independent reflections; R_{int}	9469; 0.071	7461; 0.055
Reflections with $I > 2\sigma(I)$	7902	5294
Number of parameters	380	323
$R(F)$ [$I > 2\sigma(I)$reflns]	0.0359	0.0339
$wR(F^2)$ (all data)	0.0848	0.0920
GOF(F^2)	1.147	1.037
$\Delta\rho_{max,\ min}$ (e Å^{-3})	1.21, −1.05	1.63, −0.88

3 Results and Discussion

3.1 Synthetic Aspects

Triorganotin(IV) complexes Me_3SnLH (**1**) and Ph_3SnLH (**2**) were prepared by reacting sodium salt (LHNa) with R_3SnCl (R = Me or Ph) in 1:1 molar ratios in anhydrous

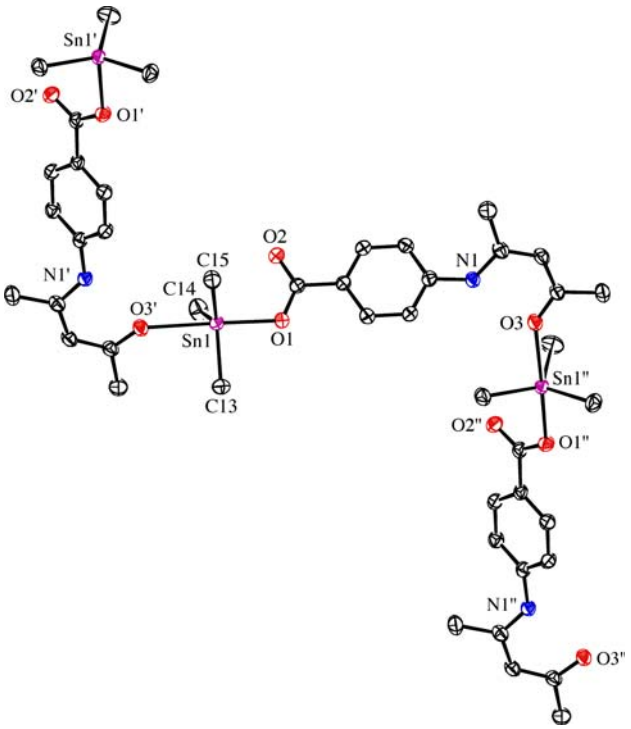


Fig. 1 Three repeats of one of the two crystallographically and chemically unique units (strand A) in the polymeric $[Me_3SnLH]_n$ chain structure of **1** (50% probability ellipsoids). The H-atoms have been omitted for clarity. The other symmetry-independent polymeric strand (B, not shown) is almost identical. Symmetry codes: (′) $x, \frac{3}{2} - y, z$; (″) $x, \frac{3}{2} - y, 1 + z$

methanol, as shown in Scheme 1. The spectroscopic properties for both the complexes are given in Sect. 2.4. The complexes were obtained in good yield and purity. They are stable in air and soluble in all common organic solvents.

3.2 Crystal Structures

The polymeric structures of compounds **1** and **2** are shown in Figs. 1 and 2 (see Scheme 1 for line diagrams), while selected geometric parameters are collected in Table 2. The crystal structures of complexes **1** and **2** are very similar and exhibit the same structural motif of a polymeric chain where a single carboxylate ligand bridges adjacent *trans*-R_3SnO_2 centres via its carboxylate and oxide O-atoms. The asymmetric unit in **2** contains one of the chemical repeat units of the polymeric Sn-compound, while one independent chemical repeat unit from each of two symmetry-independent polymeric chains (designated A and B) is present in the asymmetric unit of **1**. The primary coordination sphere of the Sn-atom is trigonal bipyramidal with the Sn–R (R = Me or Ph) ligands in the equatorial plane and the axial positions occupied by one O-atom from the carboxylate group of one ligand and the oxide O-atom (formerly the hydroxy group) of the next carboxylate ligand in the chain. In both the structures, the chains propagate in a zig-zag fashion along the crystallographic [001] direction. A polymeric structure with a similar mode of coordination and geometry about the Sn-atom was observed in the triorganotin(IV) complexes with 2-{[(*E*)-1-(2-hydroxyphenyl) methylidene]amino}acetate [12], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate [17], 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}phenylpropionate [17], 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene] amino}phenylpropionate [17], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methyl-pentanoate [27] and 2-{[(*E*)-1-(2-hydroxyphenyl)alkylidene]amino}-4-methylpentanoates [27]. In **1** and **2**, the second O-atom of the carboxylate group is not involved in the primary coordination sphere of the Sn-atom, but coordinates very weakly to the Sn-atom via long Sn···O interactions of 3.076(2) and 2.998(2) Å in chains A and B, respectively, in **1** and 2.962(2) Å in **2**, although these distances are still within the sum of the van der Waals radii of the respective atoms (ca. 3.6 Å). There are only very small distortions of the trigonal bipyramidal Sn-coordination geometry as a result of the Sn···O(2) contact (Table 2). Similar additional weak Sn···O coordination was also observed in the structures of related polymeric $[R_3SnLH]_n$ derivatives [12, 17, 27], in which the Sn···O distances are significantly longer than those observed in triphenyltin(IV) compounds **1** and **2**. The formal hydroxy group in **1** and **2** has lost its H-atom, so it is

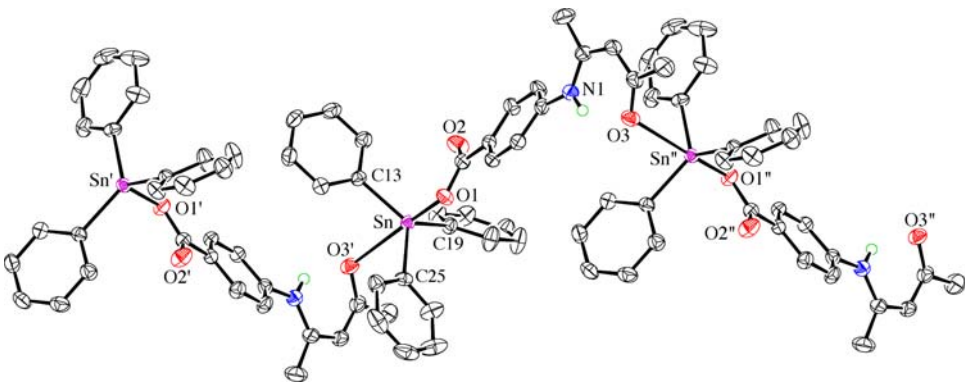


Fig. 2 Three repeats of the crystallographically and chemically unique unit in the polymeric $[Ph_3SnLH]_n$ chain structure of **2** (50% probability ellipsoids). Most H-atoms have been omitted for clarity. Symmetry codes: (′) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$; (″) $\frac{1}{2} - x, -y, \frac{1}{2} + z$

Table 2 Selected bond lengths (Å) and bond angles (°) for **1** and **2**

1A		**1**B		**2**	
Sn(1)–O(1)	2.135(2)	Sn(2)–O(4)	2.138(2)	Sn–O(1)	2.100(2)
Sn(1)–O(3′)	2.524(2)	Sn(2)–O(6′)	2.450(2)	Sn–O(3′)	2.789(2)
Sn(1)–O(2)	3.076(2)	Sn(2)–O(5)	2.998(2)	Sn–O(2)	2.962(2)
Sn(1)–C(13)	2.122(3)	Sn(2)–C(28)	2.129(3)	Sn–C(13)	2.125(2)
Sn(1)–C(14)	2.122(3)	Sn(2)–C(29)	2.126(3)	Sn–C(19)	2.122(2)
Sn(1)–C(15)	2.117(3)	Sn(2)–C(30)	2.120(3)	Sn–C(25)	2.123(2)
O(1)–C(1)	1.296(3)	O(4)–C(16)	1.300(3)	O(1)–C(1)	1.304(3)
O(2)–C(1)	1.227(3)	O(5)–C(16)	1.230(3)	O(2)–C(1)	1.221(3)
O(1)–Sn(1)–O(3′)	174.61(7)	O(4)–Sn(2)–O(6′)	176.09(8)	O(1)–Sn–O(3′)	166.84(6)
O(1)–Sn(1)–C(13)	89.8(1)	O(4)–Sn(2)–C(28)	92.0(1)	O(1)–Sn–C(13)	100.13(8)
O(1)–Sn(1)–C(14)	100.0(1)	O(4)–Sn(2)–C(29)	98.31(9)	O(1)–Sn–C(19)	103.25(8)
O(1)–Sn(1)–C(15)	96.7(1)	O(4)–Sn(2)–C(30)	96.2(1)	O(1)–Sn–C(25)	89.17(8)
C(13)–Sn(1)–O(3′)	87.78(9)	C(28)–Sn(2)–O(6′)	87.7(1)	C(13)–Sn–O(3′)	79.85(7)
C(14)–Sn(1)–O(3′)	85.4(1)	C(29)–Sn(2)–O(6′)	78.29(9)	C(19)–Sn–O(3′)	88.00(7)
C(15)–Sn(1)–O(3′)	80.24(9)	C(30)–Sn(2)–O(6′)	87.5(1)	C(25)–Sn(1)–O(3′)	79.89(7)
C(13)–Sn(1)–C(14)	116.8(1)	C(28)–Sn(2)–C(29)	113.3(1)	C(13)–Sn–C(19)	118.95(9)
C(13)–Sn(1)–C(15)	117.8(1)	C(28)–Sn(2)–C(30)	115.0(1)	C(13)–Sn–C(25)	121.94(9)
C(14)–Sn(1)–C(15)	122.6(1)	C(29)–Sn(2)–C(30)	128.7(1)	C(19)–Sn–C(25)	114.00(9)

Symmetry codes for primed atoms are: **1**A $x, \frac{3}{2} - y, z$; **1**B $x, \frac{1}{2} - y, z$; **2** $\frac{1}{2} - x, -y, -\frac{1}{2} + z$.

negatively charged. Instead the N-atom of the C=N group is protonated, thus leading to a zwitterionic ligand. In each zwitterionic carboxylate ligand, the protonated N-atom forms an intramolecular hydrogen bond with the oxide O-atom of the same ligand to give a six-membered loop with a graph set motif [28] of S(6).

3.3 Spectroscopy

The structures of the complexes **1** and **2** were further confirmed from the Mössbauer spectra in the solid-state and the results are in excellent agreement with the structures determined from X-ray crystallography (see Sect. 3.2). The spectra show a characteristic doublet absorption with narrow line width, Γ, indicating the occurrence of unique tin coordination sites in both the compounds. The isomer shift (δ) values of $\sim$1.30 mm s^{-1} are typical of quadrivalent organotin derivatives [29]. The quadrupole splitting (Δ) values for **1** and **2** are in the characteristic range for a trigonal bipyramidal geometry with the R groups in equatorial positions and axial electronegative ligands [29, 30]. The Δ values for the trimethyltin(IV)- and triphenyltin(IV) compounds **1** and **2** also match closely with the values found for the trimethyltin(IV) 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate [12] and triphenyltin(IV) complexes with 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}acetate [12], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate [17], 2-{[(*E*)-1-(2-hydroxyphenyl)methylidene]amino}-phenylpropionate [17], 2-{[(*E*)-1-(2-hydroxyphenyl)ethylidene]amino}phenylpropionate [17], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methyl-pentanoate [27], 2-{[(*E*)-1-(2-hydroxyphenyl)alkylidene]amino}-4-methyl-pentanoates [27], respectively, which were previously characterized crystallographically.

The solid-state IR spectra of complexes **1** and **2** display a medium intensity band at around 3370 cm^{-1} which has been assigned to a *v*NH vibration, consistent with the complexes existing in the keto-enamine form, in accord with our earlier report [19]. This is also reflected in the crystal structures determined (vide supra). A strong sharp band due to the [v_{asym}(OCO)] stretching vibration of the free ligand (LHH′) at 1699 cm^{-1} is shifted to $\sim$1636 cm^{-1} in **1** and **2** as a result of carboxylate coordination to the Sn atom [10, 14, 16, 17, 19].

The ^{1}H and ^{13}C NMR signals of LHH′ were assigned by the use of homonuclear correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond connectivities (HMBC) experiments [19]. The conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes owing to the data similarity. The ^{1}H and ^{13}C chemical shift assignment (Sect. 2.4) of the organotin moiety is straightforward from the multiplicity patterns and resonance intensities. The ^{1}H NMR integration values were completely consistent with the formulation of the products. The ^{13}C NMR spectra of the ligand and Sn-R skeletons displayed the expected carbon signals in all cases. The solution-state structures of complexes **1** and **2** were derived

from ^{119}Sn NMR chemical shifts, which are summarized in Sect. 2.4. The $[R_3Sn(LH)]_n$ (**1** and **2**) in $CDCl_3$ exhibit a single sharp resonance at around 134 ppm (R = Me) and −111 ppm (R = Ph) suggesting the Sn-center has a four-coordinate environment [12, 16, 27, 31–33]. The δ values, shifted downfield with respect to the analogous triorganotin(O_2-donor pyrazolonate) [33] complexes, testify that the polymeric structures of **1** and **2**, revealed in the crystal structures, are not retained in solution and that LH acts in solution as a monodentate O-donor, likely through the carboxylate arm.

4 Supplementary Materials

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC-725435 (**1**) and CCDC-725436 (**2**). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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